

PTO 09-4553

CC=JP
DATE=20010417
KIND=KOKAI
PN=2001106967

AQUEOUS COATING COMPOSITION AND COATED ARTICLE COATED
THEREWITH
[SUISEI TORYO SOSEIBUTSU OYOBI KONO SOSEIBUTSU WO TOSO
SHITA TOSOBUPPIN]

KAZUTO YAMAMOTO ET AL

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. APRIL 2009
TRANSLATED BY: SCHREIBER TRANSLATION, INC.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	2001106967
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	20010417
APPLICATION NUMBER	(21):	11282651
APPLICATION DATE	(22):	19991004
INTERNATIONAL CLASSIFICATION	(51):	C09D 167/00 5/00 5/08 133/08 B05D 7/14
PRIORITY COUNTRY	(33):	N/A
PRIORITY NUMBER	(31):	N/A
PRIORITY DATE	(32):	N/A
INVENTOR(S)	(72):	Kazuto Yamamoto Eiji Kuwano Teiji Katayama
APPLICANT(S)	(71):	Kansai Paint Co., Ltd.
DESIGNATED CONTRACTING STATES	(81):	N/A
TITLE	(54):	AQUEOUS COATING COMPOSITION AND COATED ARTICLE COATED THEREWITH
FOREIGN TITLE	[54A]:	SUISEI TORYO SOSEIBUTSU OYOBI KONO SOSEIBUTSU WO TOSO SHITA TOSOBUPPIN

[What is claimed is]

1. An aqueous coating composition which comprises (D) 5 to 50 parts by weight at least one anticorrosive pigment selected from calcium ion-exchanged amorphous silica fine particles and a magnesium compound-modified phosphate-based anticorrosive pigment and (E) 0 to 10 parts by weight a triazole compound as against 100 parts by weight total amount of film-forming resin components comprising (A) 50 to 100 parts by weight at least one aqueous resin selected from an aqueous alkyd resin and an aqueous epoxy ester resin, (B) 0 to 50 parts by weight an aqueous acrylic resin and (C) 5 to 40 parts by weight a curing agent, characterized in that the inter-crosslink molecular weight of the cured coated film provided by said coating is in a range of from 500 to 1,500.
2. The composition according to Claim 1, characterized in that it further comprises 1 to 50 parts by weight at least one non-chromium type anticorrosive pigment selected from a zinc compound and a molybdate compound as against 100 parts by weight total amount of the film-forming resin components.
3. The composition according to either Claim 1 or 2, characterized in that it further comprises 0.1 to 20 parts by weight a phosphate group-containing acryl resin as

against 100 parts by weight total amount of the film-forming resin components.

4. A coated article using an aluminum-plated steel sheet as a substrate which is obtained by forming the cured film of the aqueous coating composition described in any of Claims 1 through 3 on an aluminum-plated steel sheet which may have been subjected to a chemical conversion treatment and/or an organic film-coating treatment.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to an aqueous coating composition which shows excellent anticorrosive properties without containing poisonous heavy metals and to a coated article which uses, as a substrate, an aluminum-plated steel sheet which is coated with the above coating composition.

[0002]

[Prior Art and Problem to be Solved by the Invention]

Conventional practice has been to use a lead-tin alloy-plated steel sheet (turn sheet) as a gasoline tank material, but the use of an aluminum-plated steel sheet instead of such a turn sheet has been considered from the standpoint of the global environmental protection, such as using no poisonous lead.

[0003] The coatings for the current turn sheet pose a problem in that, when both solvent-type and aqueous coatings are applied without modifying the composition to an aluminum-plated steel sheet, the anticorrosive properties can be significantly impaired as compared with the case where such coatings are applied to a turn sheet. In order to solve the above-described problem, the use of anticorrosive agents which are based on poisonous heavy metals chromium and lead can be considered, but the use of a large amount of an anticorrosive agent containing a poisonous heavy metal does not support the object of the global environmental protection. In addition, solvent-type coatings are not preferred also from the standpoint of the emission regulation of CO₂ gas for the purpose of preventing the global warming.

[0004] The present inventors conducted intensive research in order to obtain an aqueous coating which formed a coated film having excellent anticorrosive properties on an aluminum-coated steel without using a poisonous heavy metal-containing anticorrosive agent and, as a result, discovered that the above-described object could be attained by a coating obtained by combining calcium ion-exchanged silica fine particles, a magnesium compound-modified phosphate-based anticorrosive pigment and an

optional triazole compound with a specific aqueous resin, with the inter-crosslink molecular weight of the cured coated film provided by the coating being in a specific range. The present invention was thus completed.

[0005]

[Means of Solving the Problems] More specifically, the present invention intends to provide an aqueous coating composition which comprises (D) 5 to 50 parts by weight at least one anticorrosive pigment selected from calcium ion-exchanged amorphous silica fine particles and a magnesium compound-modified phosphate-based anticorrosive pigment and (E) 0 to 10 parts by weight a triazole compound as against 100 parts by weight total amount of film-forming resin components comprising (A) 50 to 100 parts by weight at least one aqueous resin selected from an aqueous alkyd resin and an aqueous epoxy ester resin, (B) 0 to 50 parts by weight an aqueous acrylic resin and (C) 5 to 40 parts by weight a curing agent, characterized in that the inter-crosslink molecular weight of the cured coated film provided by said coating is in a range of from 500 to 1,500.

[0006] The present invention intends to further provide a coated article using an aluminum-plated steel sheet as a substrate which is obtained by forming the cured film of the above-described aqueous coating composition on an

aluminum-plated steel sheet which may have been subjected to a chemical conversion treatment and/or an organic film-coating treatment.

[0007]

[Modes of Implementing the Invention] The components of the inventive coating composition are described in greater detail below.

[0008] (A) Aqueous resin: The aqueous resin used as component (A) in the inventive composition is at least one resin selected from an aqueous alkyd resin and an aqueous epoxy ester resin. In the present invention, the term "aqueous" refers to "water-soluble" or "water-dispersible".

[0009] The aqueous alkyd resin is not particularly restricted as long as it can be obtained by esterifying polybasic acid components, polyalcohol components and oil fatty acids, is water-based and has film-forming properties.

[0010] Examples of the main components for the above-mentioned polybasic acid components include one or more dibasic acids, such as phthalic anhydride, isophthalic acid, terephthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic acid, succinic acid, fumaric acid, adipic acid, sebacic acid and maleic anhydride, and a lower alkyl ester thereof, and three- or more polybasic acids, such as

trimellitic anhydride, methylcyclohexene tricarboxylic acid and pyromellitic acid anhydride, can be optionally used.

/3

Further, a monobasic acid, such as benzoic acid, crotonic acid and p-t-butylbenzoic acid, can be additionally used as an acid component for the purpose of adjusting the molecular weight.

[0011] Examples of the main components for the above-mentioned polyalcohol components include dihydric alcohols, such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, neopentylglycol, 3-methylpentaneglycol, 1,4-hexanediol and 1,6-hexanediol, and trihydric or higher alcohols, such as glycerol, trimethylolpropane, trimethylolpropane and pentaerythritol, can be optionally used. These polyalcohols can be used alone or in combination of two or more. Further, the above-mentioned acid components and alcohol components can be partially substituted with oxyacid components, such as dimethylol propionic acid, oxypivalic acid and parahydroxybenzoic acid, a lower alkyl ester thereof, and lactones, such as ϵ -caprolactone.

[0012] Examples of the above-mentioned oil fatty acids include coconut oil fatty acid, soybean oil fatty acid, flaxseed oil fatty acid, safflower oil fatty acid, tall oil

fatty acid, dehydrated castor oil fatty acid and tung oil fatty acid. The oil length of the alkyd resin is 30% or less and is preferably in a range of from 5 to 20%.

[0013] The esterifying reaction (including ester exchange reaction) of these components can be conducted by a conventional method.

[0014] The alkyd resin according to the present invention includes epoxy-modified alkyd resins obtained by partially esterifying an epoxy compound which is used as an alcohol component, and vinyl-modified alkyd resins obtained by graft-polymerizing a vinyl monomer, such as styrene, to an alkyd resin.

[0015] Examples of methods for converting an alkyd resin into an aqueous alkyd resin include a method wherein an alkyd resin having a high acid number is neutralized with a basic compound, such as amine compounds, thereby obtaining an aqueous alkyd resin, a method wherein a hydrophilic group, such as polyoxyethylene group is introduced into an alkyd resin so that the hydrophilic group allows the alkyd resin to be self-emulsified in water, a method wherein an alkyd resin is forcibly stirred in water in the presence of an emulsifier so that the alkyd resin can be dispersed in water, and a mixed method thereof.

[0016] The molecular weight of the resin in the aqueous alkyd resin is not particularly restricted but, in general, the number average molecular weight is preferably in a range of from 2,000 to 10,000 and the hydroxyl value is preferably in a range of from 20 to 200 mg KOH/g.

[0017] Examples of commercially available aqueous alkyd resins include Residrol VWA 5477, Residrol VWA 5499, Residrol AX 246W, Residrol AX 906W (manufactured by Vianova Co.), Watersole BC-3010, Watersole S-118 and Watersole S-346 (manufactured by Dainippon Ink & Chemicals, Inc.)

[0018] The aqueous epoxy ester resin used as component (A) is a resin in which an epoxy resin and an acid component are linked via an ester bond and which is stably dissolved or dispersed in water.

[0019] Examples of the aqueous epoxy ester resin include: an aqueous epoxy resin that can be obtained by dispersing a partially reacted product having excess carboxyl groups obtained by allowing a carboxyl group-containing polymer, such as an acryl resin, to react with an epoxy resin in an aqueous medium in the presence of ammonia or amine (e.g., Japanese Unexamined Patent Publication No. S54-75460, Japanese Unexamined Patent Publication No. S55-3481 and Japanese Unexamined Patent Publication No. S55-3482); an aqueous epoxy resin that can be obtained by polymerizing an

adduct having a polymerizable unsaturated double bond and a monomer mixture containing (meth)acrylic acid in the molecule obtained by allowing an epoxy resin to partially react with a carboxyl group-containing polymerizable unsaturated compound, such as (meth)acrylic acid so that the carboxyl group of the polymer in the monomer mixture is neutralized with a basic compound and is dispersed in an aqueous medium (see, Japanese Unexamined Patent Publication No. S57-105418 and Japanese Unexamined Patent Publication No. S58-198513); and an aqueous epoxy resin that can be obtained by neutralizing the carboxyl group of a resin obtained by allowing an epoxy resin to react with a dibasic acid, such as succinic acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, dodecandioic acid and hexahydrophthalic acid, and dispersing it in an aqueous medium.

[0020] Examples of the above-mentioned epoxy resin include bisphenol-type epoxy resins and novolac-type epoxy resins. The bisphenol-type epoxy resins can be either a resin which can be obtained, for example, by condensing epichlorohydrin and bisphenol to a high molecular weight, as needed, in the presence of an alkali catalyst, or a resin which can be obtained, for example, by condensing epichlorohydrin and bisphenol in order to obtain an epoxy resin having a low

molecular weight and subjecting the resulting low molecular weight epoxy resin and bisphenol to a polyaddition reaction. [0021] Examples of the above-mentioned bisphenol include bis(4-hydroxyphenyl)methane [bisphenol F], 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane [bisphenol A], 2,2-bis(4-hydroxyphenyl)butane [bisphenol B], bis(4-hydroxyphenyl)-1,1-isobutane, bis(4-hydroxy-tert-butyl-phenyl)-2,2-propane, p-(4-hydroxyphenyl)phenol, oxybis(4-hydroxyphenyl), sulfonylbis(4-hydroxyphenyl), 4,4'-dihydroxybenzophenone, bis(2-hydroxynaphtyl)methane, with bisphenol A and bisphenol F being particularly preferred. The above-mentioned bisphenols can be used alone or as a mixture consisting of two or more thereof.

/4

[0022] Examples of commercially available bisphenol-type epoxy resins include: products by Yuka-Shell Epoxy Co., Ltd., such as Epikote 828 (epoxy equivalent: approximately 190; number average molecular weight: approximately 350), Epikote 812 (epoxy equivalent: approximately 150; number average molecular weight: approximately 320), Epikote 815 (epoxy equivalent: approximately 180; number average molecular weight: approximately 350), Epikote 820 (epoxy equivalent: approximately 190; number average molecular weight: approximately 350), Epikote 834 (epoxy equivalent:

approximately 250; number average molecular weight: approximately 470), Epikote 1001 (epoxy equivalent: approximately 490; number average molecular weight: approximately 900), Epikote 1004 (epoxy equivalent: approximately 950; number average molecular weight: approximately 1400), Epikote 1007 (epoxy equivalent: approximately 1,700; number average molecular weight: approximately 2,900), Epikote 1009 (epoxy equivalent: approximately 3,500; number average molecular weight: approximately 3,750), Epikote 1010 (epoxy equivalent: approximately 4,500; number average molecular weight: approximately 5,500); Araldite AER 6099 manufactured by Chiba Geigy Co. (epoxy equivalent: approximately 3,500; number average molecular weight: approximately 3,800); and Epomik R-309 manufactured by Mitsui Chemicals (epoxy equivalent: approximately 3,500; number average molecular weight: approximately 3,800).

[0023] Examples of novolac-type epoxy resins that can be used as an epoxy resin include various novolac-type resins, such as phenol novolac-type epoxy resin, cresol novolac-type epoxy resin, and phenol glyoxal-type epoxy resin.

[0024] The number average molecular weight and the hydroxyl value of the aqueous epoxy ester resin used as component (A) in the inventive composition are not particularly

restricted, but in usual cases, from the standpoint of adjusting the inter-crosslink molecular weight of the resulting cured coated film to be a specific range, the number average molecular weight is preferably in a range of from 2,000 to 10,000 and the hydroxyl value is preferably in a range of from 20 to 200 mg KOH/g.

[0025] (B) Aqueous acrylic resin: In the inventive composition, the aqueous acrylic resin (B) is a water-soluble or water-dispersible acrylic resin and examples of such an aqueous acrylic resin include a water-soluble or water-dispersible acrylic resin that can be obtained by neutralizing a carboxyl group-containing acrylic resin, obtained by polymerizing it in an organic solvent, by a basic compound, such as an amine compound, and converting the resulting acrylic resin into aqueous, and an acrylic resin water dispersion obtained by emulsion polymerization. The aqueous acrylic resin (B) is a resin that can be optionally incorporated into the inventive composition.

[0026] The aqueous acrylic resin (B) is a copolymer resin consisting of a carboxyl group-containing polymerizable unsaturated monomer and other polymerizable unsaturated monomers as monomer components.

[0027] Examples of the carboxyl group-containing polymerizable unsaturated monomer include a mixture of one

or more compounds selected from acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid.

[0028] The above-mentioned other polymerizable unsaturated monomers can be any monomers which can be copolymerized with the carboxyl group-containing polymerizable unsaturated monomer and can be appropriately selected according to the required properties; known examples of such polymerizable unsaturated monomers include a mixture of one or more compounds selected from: aromatic vinyl monomers, such as styrene, vinyl toluene, 2-methyl styrene, t-butyl styrene and chlorostyrene; C1-18 alkyl esters or cycloalkyl esters, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-, i- or t-butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, decyl acrylate, lauryl acrylate, cyclohexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-, i- or t-butyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, lauryl methacrylate and cyclohexyl methacrylate; C2-8 hydroxy alkyl esters, such as 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, 3-hydroxypropylacrylate, hydroxybutylacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, 3-

hydroxypropylmethacrylate and hydroxybutylmethacrylate; and N-substituted acrylamides or N-substituted methacrylamide monomers, such as N-methylolacrylamide, N-butoxymethylacrylamide, N-methoxymethylacrylamide, N-methylolmethacrylamide and N-butoxymethylmethacrylamide.

[0029] The above-mentioned monomer components are subjected to a conventional polymerization method, such as solution polymerization and emulsion polymerization, in order to obtain a copolymer. Copolymers obtained by solution polymerization can be aqueous by neutralizing them with a basic compound. The molecular weight of the aqueous acrylic resin (B) is not particularly restricted, but in usual cases, the number average molecular weight is preferably in a range of from 5,000 to 100,000 and the hydroxyl value is preferably in a range of from 20 to 200 mg KOH/g.

(C) Curing agent: The curing agent used as component (D) in the inventive component reacts with the aqueous resin (A) and the optional aqueous acrylic resin (B), and can be dissolved or dispersed in the inventive composition; known examples of such a curing agent include aqueous melamine resins, blockisocyanate compounds and tris(alkoxycarbonylamino)triazine.

[0030] Of methylolated amino resins obtained by a reaction of a melamine with aldehydes and etherified amino resins

obtained by etherifying the methylolated amino resin with an appropriate alcohol, those which have water solubility or water dispersibility can be used as the aqueous melamine resins.

/5

Examples of the aldehydes that can be used in the above-mentioned reaction include formaldehyde, paraformaldehyde, acetaldehyde and benzaldehyde. Examples of alcohols that can be used for the above etherifying reaction include methyl alcohol, ethyl alcohol, n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, and i-butyl alcohol, with methyl alcohol being particularly preferred.

[0031] Specific examples of the aqueous melamine resin (C) include: methyl etherified melamine resins, such as CYMEL 300, 303, 325, 327, 350 and 370 [manufactured by Mitsui Cytec Co., Ltd.], NIKARAK MS15, MS17, MX430 and MX650 [manufactured by Sanwa Chemical Co., Ltd.], SUMIMAL M-55 [manufactured by Sumitomo Chemical Co., Ltd.], Resimene 740 and 741 [manufactured by Monsanto Chemical Co., Ltd.]; and methyl ether/butyl ether mixture etherified melamine resins, such as CYMEL 202, 235, 238, 254, 272 and 1130 [manufactured by Mitsui Cytec Co., Ltd.], NIKARAK MX485 and MX487 [manufactured by Sanwa Chemical Co., Ltd.], and Resimene 755 [manufactured by Monsanto Chemical Co., Ltd.]

The melamine resins can be used alone or as a mixture consisting of two or more thereof.

[0032] The blocked polyisocyanate compounds can be obtained by blocking the isocyanate group of the following polyisocyanate compounds by using a blocking agent.

[0033] Examples of polyisocyanate compounds prior to blocking include: aliphatic diisocyanates, such as lysine diisocyanate, hexamethylene diisocyanate, and trimethylhexane diisocyanate; alicyclic diisocyanates, such as hydrogenated xylylene diisocyanate, isophorone diisocyanate, methylcyclohexane-2,4 (or 2,6)-diisocyanate, 4,4'-methylene bis(cyclohexylisocyanate) and 1,3-(isocyanatomethyl)cyclohexane; aromatic diisocyanates, such as tolylene diisocyanate, xylylene diisocyanate, and diphenylmethane diisocyanate; organic polyisocyanates, such as tri- or higher polyisocyanates, such as lysine triisocyanate; adducts of such organic polyisocyanates with polyhydric alcohols, low-molecular-weight polyester resins, water or the like; and cyclopolymers (e.g., isocyanurate), biuret adducts or the like of such organic polyisocyanates.

[0034] Preferred examples of the blocking agent used for blocking the polyisocyanate compounds include: phenols, such as phenol, cresol and xylenol; lactams, such as ϵ -caprolactam, δ -valerolactam, γ -butyrolactam and β -

propylolactam; alcohols, such as methanol, ethanol, n- or i-propylalcohol, n-, i- or t-butylalcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol monomethyl ether and benzyl alcohol; oximes, such as formamidoxime, acetoamidoxime, acetoxime, methylethylketoxime, diacetylmonoxime, benzophenone oxime and cyclohexane oxime; and active methylene types, such as dimethyl malonate, diethyl malonate, ethyl acetoacetate, methyl acetoacetate and acetylacetone. The isocyanate group of the polyisocyanate can be readily blocked by mixing the above-mentioned polyisocyanate to be blocked and the above-mentioned blocking agent. The above-mentioned blocked polyisocyanate compounds can be used alone or in combination of two or more.

[0035] The three alkoxy groups in one molecule of tris(alkoxycarbonylamino)triazine that can be used as a curing agent (C) may be different from each other or the same and represent a hydrocarbon group having 1 to 20 carbon atoms, preferably 1 to 4 carbon atoms, and examples of commercially available tris(alkoxycarbonylamino)triazine include TACT (tradename, manufactured by Mitsui Cytec Co., Ltd.)

[0036] In the inventive composition, the cured coated film formed of the inventive composition preferably has an inter-crosslink molecular weight of 500 to 1500, preferably 700 to 1000. The aqueous resin (A), the aqueous acrylic resin (B) and the curing agent (C) must be appropriately selected so that the cured coated film has an inter-crosslink molecular weight to be within the above-stated range. If the inter-crosslink molecular weight exceeds 1500, the anticorrosive properties of the resulting coated film may be impaired, whereas if the inter-crosslink molecular weight is less than 500, the resulting coated film may become brittle, resulting in the impact resistance being impaired.

[0037] From the standpoint of curability and anticorrosive properties, the preferred proportion of each aqueous resin (A), aqueous acrylic resin (B) and curing agent (C) in 100 parts by weight of the total solid content are as follows: 50 to 100 parts by weight the aqueous resin (A), preferably 60 to 90 parts by weight; 0 to 50 parts by weight the aqueous acrylic resin (B), preferably 0 to 40 parts by weight; and 0 to 40 parts by weight the curing agent (C), preferably 0 to 30 parts by weight.

(D) Anticorrosive pigment: In the inventive composition, the anticorrosive pigment used as component (D) is at least

one pigment selected from calcium ion-exchanged amorphous silica fine particles and a magnesium compound-modified phosphate-based anticorrosive pigment.

/6

[0038] The calcium ion-exchanged amorphous silica fine particles (which may be referred to as "ion-substituted silica", hereinafter) are silica fine particles in which calcium ion is introduced into a microporous silica carrier by ion-exchange. It is assumed that the ion-exchanged silica which has been incorporated into the coated film is exchanged with H^+ ion which has penetrated through the coated film and Ca^{2+} ion, which is an anticorrosive ion, is emitted, thereby protecting the metal surface. Examples of commercially available ion-exchanged silica include SHELDEX (tradename) C-303, AC-3 and C-5 (manufactured by W. R. Grace & Co.).

[0039] The magnesium compound-modified phosphate-based anticorrosive pigment (which may be referred to as "modified phosphate pigment", hereinafter), which is an anticorrosive pigment consisting of a poorly water-soluble condensed phosphate, or a phosphoric acid-based layered compound, and a magnesium compound, is non-polluting anticorrosive pigment without containing poisonous metals and is an effective component for improving the

anticorrosive properties of the aluminum-plated steel sheet in the present invention.

[0040] Preferred examples of the poorly water-soluble condensed phosphate which constitutes the modified phosphate pigment include condensed phosphates which are conventionally used as anticorrosive pigments and have a solubility in water of 10 g per 1 L of water or less where the amount of phosphorous (P) is converted into P_2O_5 . Typical examples of poorly water-soluble condensed phosphate include: pyrophosphates, such as aluminum pyrophosphate, calcium pyrophosphate, tin pyrophosphate, cerium pyrophosphate, copper pyrophosphate, iron pyrophosphate, titanium pyrophosphate, magnesium pyrophosphate and manganese pyrophosphate; tripolyphosphates, such as aluminum dihydrogen tripolyphosphate and iron tripolyphosphate; and metaphosphates, such as aluminum metaphosphate, iron metaphosphate, calcium metaphosphate, tin metaphosphate, cerium metaphosphate, manganese metaphosphate, molybdenum metaphosphate and silver metaphosphate, and aluminum dihydrogen tripolyphosphate and aluminum metaphosphate are particularly preferred from the standpoint of properties such as anticorrosive properties.

[0041] Examples of the phosphoric acid-based layered compound which constitutes the modified phosphate pigment include acid salts that can be represented by the formula: $M(HPO_4)_2 \cdot XH_2O$ [wherein M represents a tetravalent metal, such as Ce, Ti, Zr and Sn, and X represents an integer of from 0 to 2] of layered phosphate of tetravalent metals. Typical examples of the phosphoric acid-based layered compound include layered cerium phosphate, layered titanium phosphate, layered zirconium phosphate and layered tin phosphate.

[0042] Examples of the magnesium compounds which constitute the modified phosphate pigment by modifying the poorly water-soluble condensed phosphate or the phosphoric acid-based layered compound include: inorganic magnesium salts, such as magnesium oxide, hydrous magnesium oxide, magnesium carbonate, basic magnesium carbonate, magnesium phosphate, magnesium borate, magnesium metaborate, magnesium silicate; and organic magnesium salts, such as magnesium stearate and organic magnesium sulfonate, with magnesium oxide, hydrous magnesium, magnesium carbonate and magnesium borate being particularly preferred.

[0043] The weight ratio of the poorly water-soluble condensed phosphate or the phosphoric acid-based layered compound to the magnesium compound in the modified

phosphate pigment is preferably in a range of from 10/1 to 10/10, as the former/the latter, from the standpoint of anticorrosive properties, improving effect of the coating stability by neutralizing pH or the like.

[0044] The modified phosphate pigment comprising the poorly water-soluble condensed phosphate, or the phosphoric acid-based layered compound, and the magnesium compound can be prepared by mixing the both components by dry-mixing or wet-mixing.

[0045] The proportion of the anticorrosive pigment (D) is preferably in a range of from 5 to 100 parts by weight, preferably 10 to 60 parts by weight, as against 100 parts by weight of the total amount of the film-forming resin components (A), (B) and (C) from the standpoint of the anticorrosive properties at the ordinary portions and the edge portions of the aluminum-plated steel sheet coated with the inventive coating composition and the water proofness of the coated film. In particular, it is preferred that the proportion of the ion-exchanged silica is in a range of from 5 to 50 parts by weight, preferably in a range of from 10 to 30 parts by weight, and the proportion of the modified phosphate pigment is in a range of from 5 to 50 parts by weight, preferably in a range of from 10 to 30 parts by weight.

[0046] (E) Triazole compound: The inventive compound, the triazole compound used as component (E) is an effective component for improving the anticorrosive properties at the ordinary portions and edge portions of the aluminum-plated steel sheet and the water proofness of the coated film.

[0047] Examples of the triazole compound (E) include 1,2,4-triazole, 3-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 3-mercapto-1,2,4-triazole, 5-amino-3-mercapto-1,2,4-triazole, 1H-benzotriazole, 1-hydroxybenzotriazole, 6-methyl-8-hydroxytriazolopyridazine, 6-phenyl-8-hydroxytriazolopyridazine and 5-hydroxy-7-methyl-1,3,8-triazaindolizine, with 3-mercapto-1,2,4-triazole and 5-amino-3-mercapto-1,2,4-triazole being preferred from the standpoint of the anticorrosive properties.

[0048] The proportion of the triazole compound (E) is preferably 10 parts by weight or less, preferably in a range of from 1 to 8 parts by weight,

/7

as against 100 parts by weight of the total amount of the film-forming resin components (A), (B) and (C) from the standpoint of the anticorrosive properties at the ordinary portions and the edge portions of the aluminum-plated steel sheet coated with the inventive coating composition and the water proofness of the coated film.

[0049] The inventive coating composition essentially comprises the film-forming resin components consisting of the aqueous resin (A), the optional aqueous acrylic resin (B) and the aqueous melamine resin (C), the above-specified anticorrosive pigment (D) and the optional triazole compound (E), but can optionally contain additive agents, known examples of which include: a conventional non-chromium type anticorrosive pigment except for components (D) and (E); a phosphate group-containing acryl resin; and additive agents, such as organic solvents, curing catalysts, coloring pigments, body pigments, neutralizing agents, and defoaming agents, coating surface adjusting agents and anti-settling agent, which are commonly used for coatings

[0050] At least one non-chromium type anticorrosive pigment selected from a zinc compound and a molybdate compound is preferred as a non-chromium type anticorrosive pigment that can be optionally contained and contributes to improving the anticorrosive properties. Examples of the zinc oxide, zinc phosphate, zinc phosphate-silicate, zinc aluminum phosphate, zinc calcium phosphate, calcium zinc cyanamide, zinc-treated aluminum polyphosphate, zinc calcium molybdate, zinc molybdate, zinc phosphomolybdate, and aluminum phosphomolybdate. Of these, zinc oxide, zinc phosphate and zinc calcium molybdate are particularly preferred.

[0051] When the non-chromium type anticorrosive pigment is incorporated, the proportion is in a range of from 1 to 50 parts by weight, preferably 2 to 40 parts by weight, as against 100 parts by weight of the total amount of the film-forming resin components (A), (B) and (C).

[0052] The phosphate group-containing acryl resin is a resin having a phosphate group on the side chain of the acrylic resin and can be obtained by copolymerizing a polymerizable unsaturated monomer having a phosphate group, such as 2-(meth)acryloyloxyethyl acid phosphate, with another monomer, such as alkyl esters of acrylic acid or methacrylic acid. In general, the phosphate group-containing acryl resin preferably has a weight average molecular weight of from 2,000 to 100,000. The phosphate group-containing acryl resin contributes to improving the water proofness of the coated film formed on the aluminum-plated steel sheet. When the phosphate group-containing acryl resin is incorporated, the proportion is in a range of from 0.1 to 20 parts by weight, preferably in a range of from 1 to 15 parts by weight, as against 100 parts by weight of the total amount of the film-forming resin components.

[0053] The organic solvent can be optionally incorporated in order to improve the coating performance of the

inventive composition and is preferably a hydrophilic organic solvent which allows the resins (A), (B) and (C) to be dissolved or dispersed in water; known examples of such an organic solvent include ether solvents, such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, alcohol solvents, such as methanol, ethanol, isopropanol and butanol, and acetone. These organic solvents can be used alone or in combination of two or more.

[0054] The curing catalyst can be optionally incorporated in order to promote the reaction of the aqueous resin (A) and the aqueous acrylic resin (B) with the curing agent (C). In the case where the curing agent (C) is an aqueous melamine resin, sulfonic acid compounds or an amine neutralizing product of such sulfonic acid compounds can be preferably used as a curing agent. Examples of the sulfonic acid compounds include p-toluene sulfonic acid, dodecyl benzene sulfonic acid, dinonylnaphthalene sulfonic acid, and dinonylnaphthalene disulfonic acid. The amine in the amine neutralizing product of the sulfonic acid compounds can be primary amine, secondary amine and tertiary amine. In the case where the curing agent (C) is a blocked polyisocyanate compound, examples of compounds that can be used as a curing agent include organic metal catalysts,

such as tin octoate, dibutyltin di(2-ethylhexanoate), dioctyl tin di(2-ethylhexanoate), dioctyl tin diacetate, dibutyl tin dilaurate, dibutyl tin oxide, dioctyl tin oxide and tin 2-ethylhexanoate.

[0055] When the curing is incorporated, the proportion is preferably in a range of from 0.1 to 4.0 parts by weight as against 100 parts by weight of the total amount of the film-forming resin components.

[0056] The body pigment can be appropriately selected at least one selected from baryta, calcium carbonate and a mixture crystal of calcium carbonate and magnesium carbonate according to the hardness, physical properties and adhesion of the coated film. The proportion of the body pigment is not particularly restricted, but is generally 200 parts by weight or less and is preferably in a range of from 30 to 150 parts by weight as against 100 parts by weight of the total amount of the film-forming resin components.

[0057] Next, the coating method for the inventive coating composition is described below.

[0058] The inventive composition can be applied, for example, to metals, mortar, cement, plastics and glasses, and can be preferably applied to metals and, in particular, steel sheets. Examples of the steel sheet to be coated

include cold rolled steel sheets, hot dip zinc-coated steel sheets, electrolytic zinc-coated steel sheets, alloyed zinc coated steel sheet, aluminum-plated steel sheets, stainless steel sheets, copper-plated sheets, tin-plated steel sheets, lead-tin alloy-plated steel sheets (turn sheets) and steel sheets which have been subjected to a chemical conversion treatment and/or an organic film-coating treatment, such as a phosphate treatment and a chromate treatment.

/8

Examples of the steel sheets which are subjected to a chemical conversion treatment and/or an organic film-coating treatment include the above-mentioned steel sheets which have been subjected to a chemical conversion treatment, the above-mentioned steel sheets which have been subjected to an organic film-coating treatment and the above-mentioned steel sheets which have been subjected to which have been subjected to an organic film-coating treatment after subjecting it to a chemical conversion treatment. Examples of the organic film-coating treatment include a film coating by an acryl emulsion, a film coating by a phenoxy resin, and a film coating by an epoxy resin. The thickness of the organic film in the organic film-coating treatment is not particularly restricted, but is preferably in a range of from 0.3 to 3 μm .

[0059] Aluminum plated steel sheets which may have been subjected to a chemical conversion treatment and/or an organic film-coating treatment can be particularly preferably used as a substrate. These steel sheets can be sheet-like prior to processes or can also be formed and processed.

[0060] The inventive composition can be preferably used as a undercoating or a one-coat finishing and can be applied to the above-mentioned steel sheets by a conventional method, such as a shower-coating method, a roll-coating method, a spraying method, a brushing method and a dipping method. The thickness of the resulting coating by the inventive coating composition is not particularly restricted, but in the case of the undercoating, the thickness is generally in a range of from 2 to 40 μm , preferably in a range of from 5 to 30 μm , and in the case of the one-coat finishing, the thickness is generally in a range of from 8 to 50 μm , preferably in a range of from 10 to 40 μm . The drying of the coated film of the inventive coating composition can be conducted, in the case of continuously baking the coated film by a coil coating method, generally at the maximum material temperature of 160 to 250 degrees Celsius, preferably 180 to 230 degrees Celsius, for 15 to 60 seconds, and in the case of batch-

wise baking the coated film, generally at a temperature of 80 to 160 degrees Celsius for 10 to 30 minutes.[0061] The drying of the coated film of the inventive coating composition can be conducted, in the case of continuously baking the coated film by a coil coating method, generally at the maximum material temperature of 160 to 250 degrees Celsius, preferably 180 to 230 degrees Celsius, for 15 to 60 seconds, and in the case of batch-wise baking the coated film, generally at a temperature of 80 to 160 degrees Celsius for 10 to 30 minutes.

[0062]

[Embodiments] Hereinafter, the present invention is further described in greater detail by using embodiments. The terms "part" and "%" are based on weight, unless otherwise indicated.

[0063] Preparation Example 1

An alkyd resin which had been modified by tall oil fatty acid and flaxseed oil fatty acid, had an oil length of 42% and had an acid value of 40 mg KOH/g was neutralized with an equivalent amount of triethylamine, was adjusted to a non-volatile component of 68% by using deionized water, and ethylene glycol monobutyl ether was added thereto, thereby yielding an alkyd resin aqueous solution having a content of non-volatile component of 50%.

[0064] Preparation of aqueous coating composition

Embodiments 1 to 9 and Comparative Example 4

Each aqueous coating composition having a viscosity of approximately 500 cps [measured using a Brookfield viscometer (6 rpm) at a temperature of 20 degrees Celsius] was obtained by using part of the aqueous epoxy ester A (*1, 20 parts at a solid content), mixing it with a pigment (including anticorrosive pigments) and an anticorrosive agent shown in Table 1 according to the formulation shown in Table 1, dispersing the pigment, adding the rest of the components shown in Table 1 to the resulting dispersion, and adding deionized water.

[0065] Embodiments 10 and 11 and Comparative Examples 1 to 3

Each aqueous coating composition having a viscosity of approximately 500 cps [measured using a Brookfield viscometer (6 rpm) at a temperature of 20 degrees Celsius] was obtained by using the alkyd resin aqueous solution having a content of non-volatile component of 50% obtained in the Preparation Example 1, mixing it with a pigment (including anticorrosive pigments) and an anticorrosive agent shown in Table 1 according to the formulation shown in Table 1, dispersing the pigment, adding the rest of the

components shown in Table 1 to the resulting dispersion, and adding deionized water.

[0066] The formulation shown in Table 1 is based on the non-volatile component. The "notes" shown in the following Table 1 are as follows:

(*1) Aqueous epoxy ester A: epoxy ester emulsion having a non-volatile component of 40%, a number average molecular weight of approximately 4000 and a hydroxyl value of approximately 60 mg KOH/g.

(*2) Aqueous epoxy ester B: tradename "CD 540" (manufactured by Dainippon Ink and Chemicals Inc., epoxy ester emulsion having a non-volatile component of 40%.

(*3) Aqueous melamine resin: tradename "CYMEL 325" (manufactured by Mitsui Cytec Co., Ltd.), methyletherified melamine resin.

(*4) TACT: tradename manufactured by Mitsui Cytec Co., Ltd., tris(alkoxycarbonylamino)triazine.

(*5) Blocked isocyanate compound: methylethylketoxim blocked product of triisocyanurate body of hexamethylenediisocyanate.

/9

(*6) Aqueous acrylic resin: tradename "AD 69" (manufactured by Kanebo Co., Ltd.), acrylic resin emulsion having a non-volatile component of 48%.

[0067] (*7) SHELDEX C-303: tradename manufactured by W. R. Grace & Co., calcium ion-exchanged amorphous silica fine particles.

(*8) SHELDEX AC-5: tradename manufactured by W. R. Grace & Co., calcium ion-exchanged amorphous silica fine particles.

(*9) Modified phosphate-based anticorrosive pigment: a magnesium-modified phosphate-based anticorrosive pigment obtained by wet-mixing a magnesium compound and aluminum dihydrogen tripolyphosphate.

(*10) Phosphate group-containing acryl resin: a phosphate group-containing acrylic resin having structure monomer components of styrene/n-butylacrylate/2-hydroxyethylmethacrylate/2-methacryloyloxyethylacid phosphate = 30/40/10/20 (weight ratio): the acid value of the resin is 95 mg KOH/g, the hydroxyl value is 43 mg KOH/g and the weight average molecular weight is approximately 20,000.

[0068] Measurement of inter-crosslink molecular weight
Clear coatings containing the resins obtained in Embodiments 1 to 11 and Comparative Examples 1 to 4 were prepared, respectively, were then applied to a Teflon sheet so that the thickness of the dried film could be approximately 30 μm , and were baked at a temperature of 130 degrees Celsius for 20 minutes, thereby yielding cured

clear coating films. Next, the resulting clear coating films were peeled off from the Teflon sheet in order to obtain free coated films. Each resulting clear coated film was cut into pieces having a width of 5 mm and two resulting pieces were assembled to a thickness of 60 μm in order to obtain a sample. The sample having a length of the measuring portion of 10 mm was installed in a dynamic viscoelasticity measuring device "UBM-V4" (manufactured by UBM Co., Ltd.) and the dynamic viscoelasticity was measured at a frequency of 110 Hz, a static load of 10 g and an amplitude value of 2.0 μm at a temperature increasing rate of 4 $^{\circ}\text{C}/\text{min}$. from 30 degrees Celsius to 200 degrees Celsius, thereby obtaining the inter-crosslink molecular weight. The results are shown in Table 1.

[0069] Preparation of test coated sheet

The aqueous coating compositions obtained in Embodiments 1 to 11 and Comparative Examples 1 to 4 were applied to an aluminum-plated steel sheet (tradename "ALSTARE", manufactured by Nisshin Steel Co., Ltd.) having a thickness of 1.0 mm, respectively, by a dip-coating method and were baked at a temperature of 130 degrees Celsius for 20 minutes, thereby preparing test coated sheet. The thickness of any of the resulting dried films was approximately 23 μm . The following performance tests were conducted on the

resulting test coated sheets according to the methods described below. The test results are shown in Table 1.

[0070] Testing method

Adhesiveness: in accordance with the cross-cut tape method in JIS K 5400, 8. 5. 2. (1990), 100 squares having a size of 1 mm × 1 mm were created by forming eleven parallel linear cuts on the coated surface of the test sheet vertically and transversely at an interval of 1 mm by using a cutter knife in such a way that the cuts could reach the base. Cellophane tapes were adhered to the surface and rapidly peeled off from the surface in order to observe and evaluate the removal state of the squares by the following criteria:

[0071]

○: no peeling of coating film was observed

△: slight peeling of coating film was observed, with the

number of remaining squares being 90 or more.

×: considerable peeling of coating film was observed, with the number of remaining squares being less than 90.

[0072] Anticorrosive properties: the test coated sheet was cut into pieces having a size of 75 × 150 mm and the resulting piece was subjected to a salt spray test for 840 hours in accordance with JIS Z-2371. The generation of corrosion of the ordinary portion of the resulting test coated sheet piece was visually evaluated by the following criteria, and the corrosion width of the edge (mm), which is the maximum corrosion width measured from the edge, was also measured:

[0073] Corrosion generation level on the ordinary portion
o: no generation of corrosion was observed on the ordinary portion

Δ: slight generation of corrosion was observed on the

ordinary portion

×: considerable generation of corrosion was observed on the ordinary portion

[0074] Water proofness: After the test coated sheet had been immersed in warm water at a temperature of 40 degrees Celsius for 120 hours, in accordance with the cross-cut tape method in JIS K 5400, 8. 5. 2. (1990), 100 squares

having a size of 1 mm × 1 mm were created by forming eleven parallel linear cuts on the coated surface of the test sheet vertically and transversely at an interval of 1 mm by using a cutter knife in such a way that the cuts could reach the base. Cellophane tapes were adhered to the surface and rapidly peeled off from the surface in order to count the number of remaining squares of 100 squares.

[0075]

[Table 1]

/10

Table 1

	Example No.	Embodiments										
		1	2	3	4	5	6	7	8	9	10	11
Resins	Aqueous alkylid resin											
	Aqueous epoxy ester A (*1)	80	80	80	80	80	80	80	80	80	60	80
	Aqueous epoxy ester B (*2)											
	Aqueous melamine resin (*3)	20	20	20	20	20	20	20			20	10
	TACT (*4)								20			
	Blocked isocyanate (*5)									20		
Pigments and anticorrosive agents	Aqueous acrylic resin (*6)											10
	Carbon black	10	10	10	10	10	10	10	10	10	10	10
	Calcium carbonate	20	20	20	20	20	20	20	20	20	20	20
	Zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	SHFL DEX C-303 (*7)	15		2.5	20		15	15	15	15	15	15
	SHFL DEX AC-5 (*8)		16						15			
	Modified phosphate-based anticorrosive pigment (*9)	15	15	25	-	20	15	15	15	15	15	15
	3-mercaptop-1,2,4-triazole						10					
	Phosphate group-containing acryl resin (*10)							10				
	Inter-crosslink molecular weight	880	880	880	880	880	880	880	880	880	1200	1500
Test results	Adhesion	o	o	o	o	o	o	o	o	o	o	o
	Anticorrosive properties	o	o	o	o	o	o	o	o	o	o	o
	Ordinary portion Edge portion (mm)	2.5	2.0	2.0	2.0	2.0	1.5	1.5	2.0	2.0	3.0	4.0
	Water proofness	100	100	100	100	100	100	100	100	100	100	100

[0076]

[Table 2]

Table 1 (Cont'd)

	Example No.	Comparative Examples			
		1	2	3	4
Resins	Aqueous alkylid resin	20	20	20	30
	Aqueous epoxy ester A (*1)				
	Aqueous epoxy ester B (*2)	10	30	40	
	Aqueous melamine resin (*3)	10	20	10	20
	TACT (*4)				
	Blocked isocyanate (*5)				
Pigments and anticorrosive agents	Aqueous acrylic resin (*6)			10	
	Carbon black	10	10	10	10
	Calcium carbonate	20	20	20	20
	Zinc oxide	2.5	2.5	2.5	2.5
	SHFL DEX C-303 (*7)	15	15	15	
	SHFL DEX AC-5 (*8)				
	Modified phosphate-based anticorrosive pigment (*9)	15	15	15	
	3-mercaptop-1,2,4-triazole				
	Phosphate group-containing acryl resin (*10)				
	Inter-crosslink molecular weight	3600	3800	3500	880
Test results	Adhesion	o	o	o	o
	Anticorrosive properties	o	o	o	o
	Ordinary portion Edge portion (mm)	11.0	9.0	11.0	12.0
	Water proofness	100	100	100	100

[0077]

[Effect of the Invention] The inventive coating composition, which is a water-based composition and does not contain poisonous heavy metals, is advantageous from the standpoint of the prevention of environmental pollution. The inventive aqueous coating composition forms a coated film having excellent anticorrosive properties without using poisonous heavy metals and, in particular, a coated steel sheet which can be obtained by applying the inventive aqueous coating composition to an aluminum-plated steel sheet shows remarkably preferred anticorrosive properties at ordinary portions and edge portions, with excellent water proofness.

/11

Therefore, an aluminum-plated steel sheet can be alternatively used for a turn sheet using a poisonous lead by using the inventive aqueous coating composition, which is advantageous from the standpoint of the global environmental protection.